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Advanced Chlor-Alkali Technology

Jerzy Chlistunoff

Los Alamos National Laboratory



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Project Plan

Goals

- **Improve energy efficiency** of the chlor-alkali process (by replacing hydrogen-evolving cathode with **oxygen-consuming cathode**)
- **Lower** the production **cost**
- Deliver products that would match or **exceed** current industrial **purity standards**

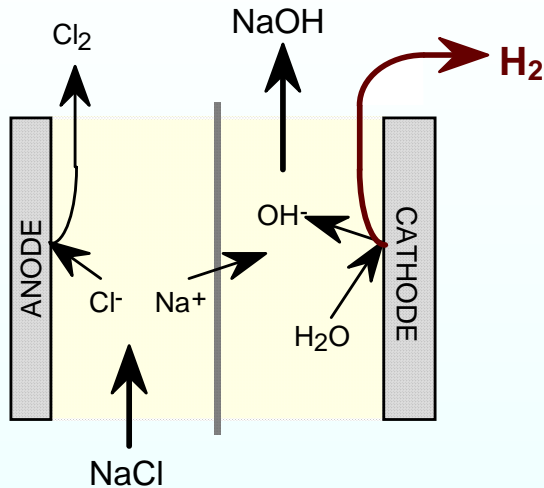
Objectives

- **Identification** of the best **materials and structures**
- **Optimization** of the operating **conditions**
- Bringing the **oxygen cathode chlor-alkali process** to the point where it will become **attractive for the industry to invest** in the process scale-up and, eventually, in the implementation of the technology



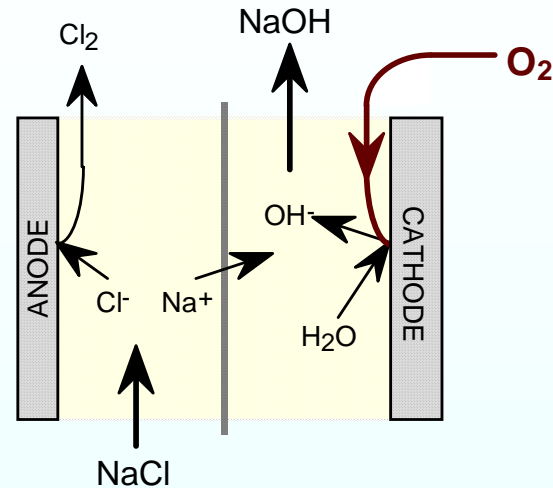
Reducing Energy Consumption in a Chlor-Alkali Reactor Using an Oxygen Cathode

a) Conventional Chlor-Alkali Cell



Typical $V_{\text{cell}} = 3.2 \text{ V}$ at 0.4 A cm^{-2}

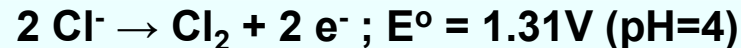
b) Chlor-Alkali Cell with Oxygen Cathode



Typical $V_{\text{cell}} = 2.3 \text{ V}$ at 0.4 A cm^{-2}

CELL REACTIONS

Anode:



Cathode:



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Energy and the Chlor-Alkali Industry

Basic Assumptions and Technical Data

Technology	% of US market	Energy Consumption kWh per 1 ton of Cl_2	NaOH Concentration %	Comments
Mercury	12	3360	50 Very pure	Environmental concerns (Hg)
Diaphragm	70	2900	12	Inexpensive cells Asbestos
Membrane	18	2500	32 Pure	Expensive cells
Oxygen cathode	0	1750	32 Pure	Expensive cells

- Potential energy recovery from H_2 : 550 kWh (PEM FC at 50% efficiency)
- Identical cost of compressing/storing O_2 /air for oxygen depolarized chlor-alkali cell and PEM FC
- Identical cost of oxygen diffusion cathodes for chlor-alkali cell and PEM FC

Energy and the Chlor-Alkali Industry

Technology	Energy/Money Savings Upon Conversion To Oxygen Cathode Technology (per 1 ton of chlorine)			Capital Cost of Conversion to Other Technology (per 1 ton of chlorine) ^{a)}		
	kWh	%	\$	Oxygen Cathode ^{b)}	Membrane ^{c)}	Conventional + PEM FC ^{d)}
Mercury	1610	48	79	\$10-80	\$10-80	\$15-120
Mercury + PEM Fuel Cell Stack	1060	38	52			
Diaphragm	1150	40	56	\$10-80		\$15-120
Diaphragm + PEM Fuel Cell Stack	600	26	29			
Membrane	750	30	37	\$10-80		\$15-120
Membrane + PEM Fuel Cell Stack	200	8	10			

- a) Conversion costs per 1 ton of chlorine calculated from conversion costs per 1 ton of chlorine capacity and plant operating life of 10-40 years
- b) Estimated
- c) *Modern Chlor-Alkali Technology*



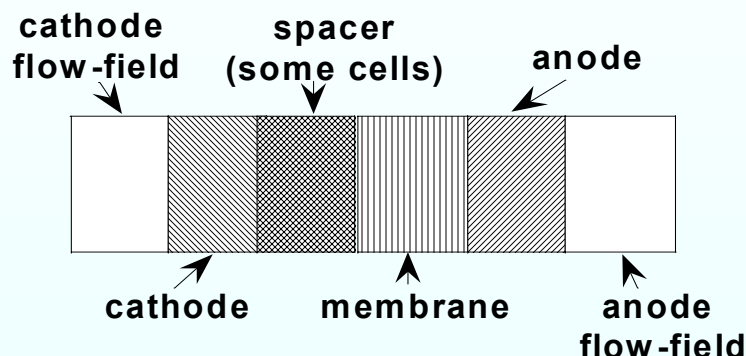
Summary of Recent Effort

- **Cathode modifications aimed at:**
 - reducing flooding susceptibility of peroxide-destroying structure
 - increasing caustic current efficiency
- **Selecting materials for the cathode hardware:**
 - determining effect of cathode hardware coating on peroxide byproduct generation
 - reducing hardware corrosion
- **Anode modifications aimed at:**
 - increasing caustic current efficiency (CCE)



Typical Experimental Conditions

- **Zero-gap cell configuration:** cell components in intimate contact (see scheme below)
- **Cathode:** 50 cm² double-sided ELAT
 - **Catalyst:** 20% Pt/C (0.5 mg/cm²)
 - **Cathode flow-field:** LANL metal patterned flow-field
 - **Carbon cloth spacer (Panex[®] 30)** between the cathode and the membrane
- **Anode:** DSA[®] coated Ti meshes (size 120 and 60)
- **Membrane:** Asahi F4232

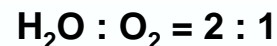


- **Oxygen:** pressure - 138 kPa (20 psig); flow - 5 times that required by stoichiometry; humidification - 0.5 cm³/min
- **Brine concentration:** 200 g/dm³
- **Temperature:** 90°C

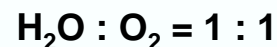
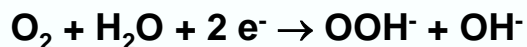
Panex[®] is a trademark of Zoltek Corporation and DSA[®] is a trademark of Eltech Systems Corporation

Processes in Alkaline Oxygen Electrode

Hydroxide Formation:



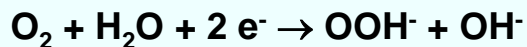
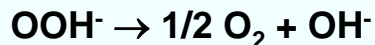
Peroxide Formation:



Peroxide precipitation:

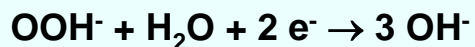


Peroxide Decomposition:

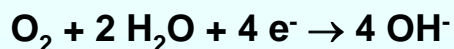


C

followed by:



Pt



Pt

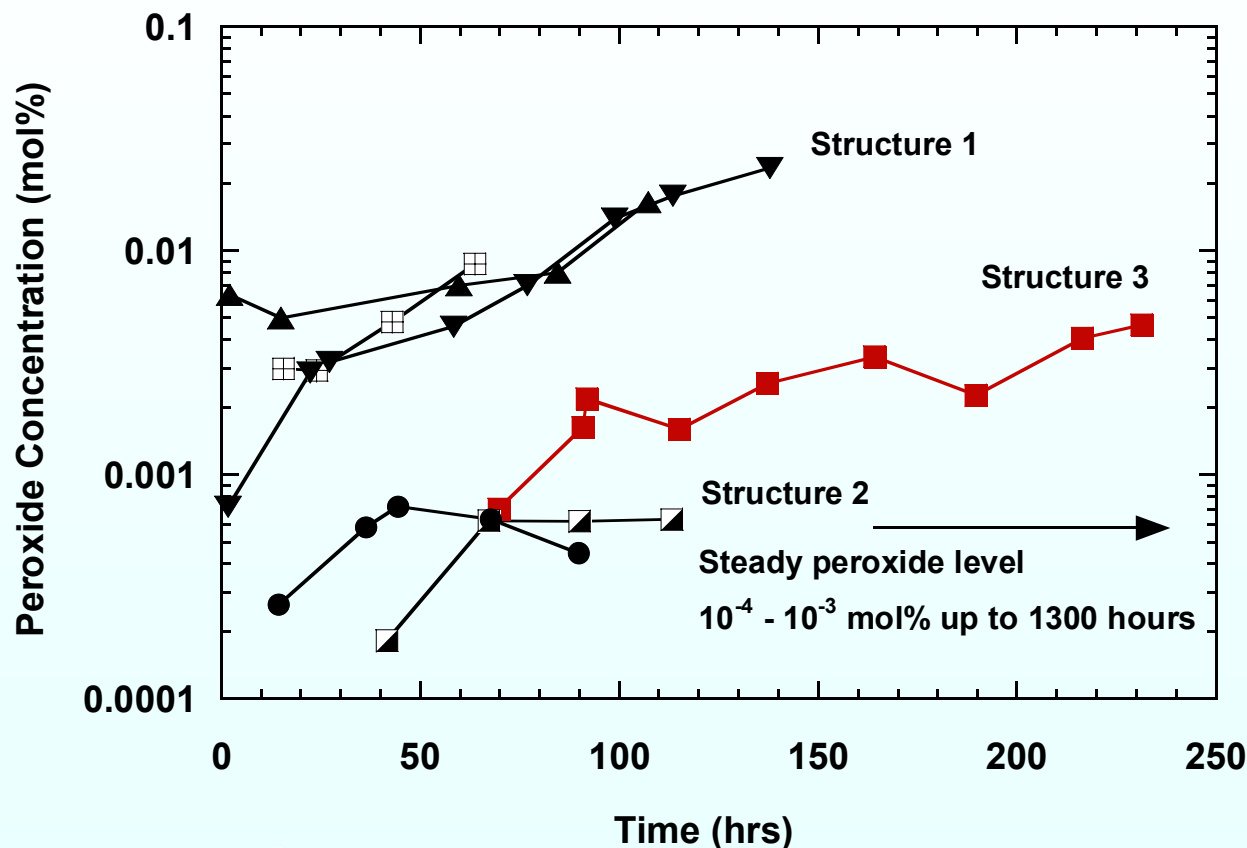


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Reduction of Flooding Susceptibility of the Peroxide-Destroying Cathode Structure

Current densities were increased stepwise from 0.2 to 1.0 A/cm² during first 70-100 hrs



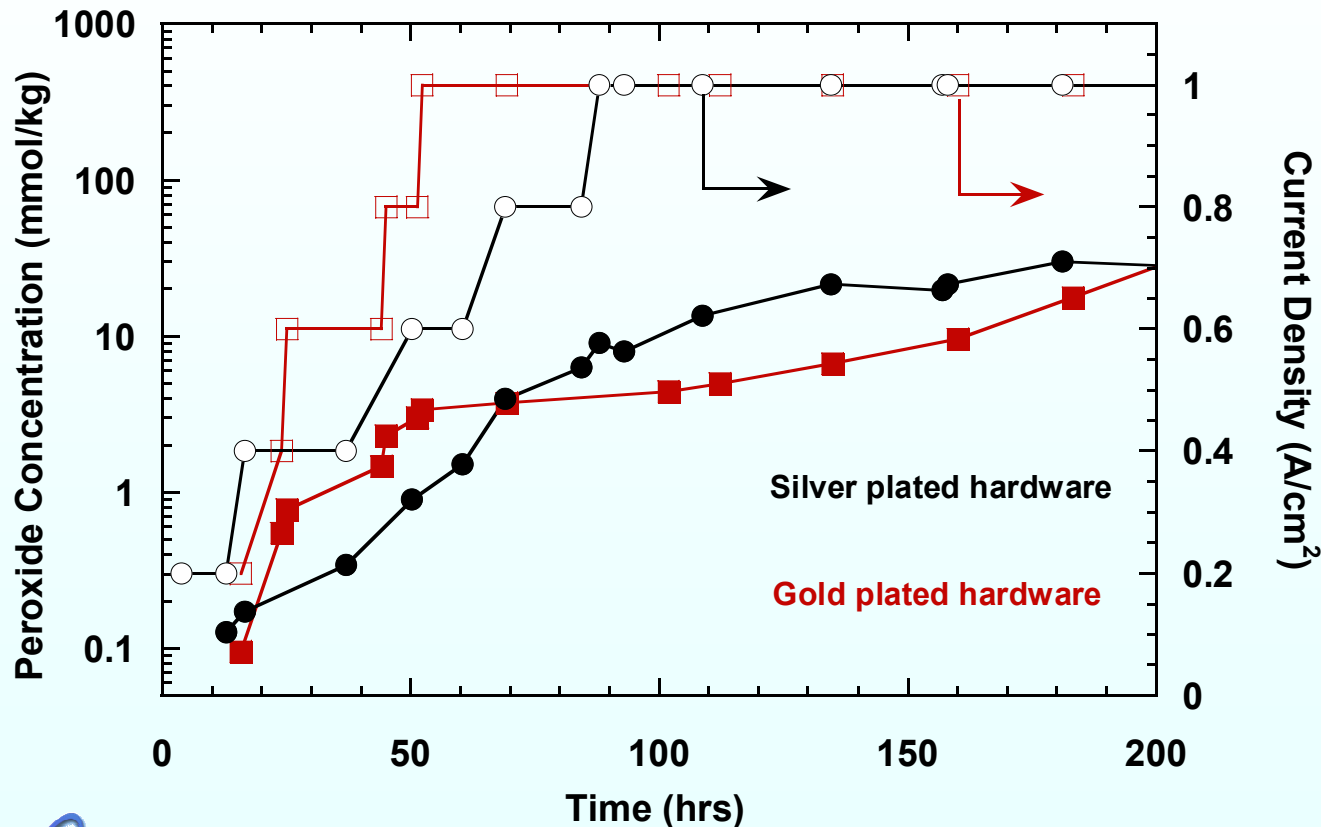
Structure 1 – reference

Structure 2 – peroxide-destroying structure, patent application

Structure 3 – reduced flooding, increased peroxide generation

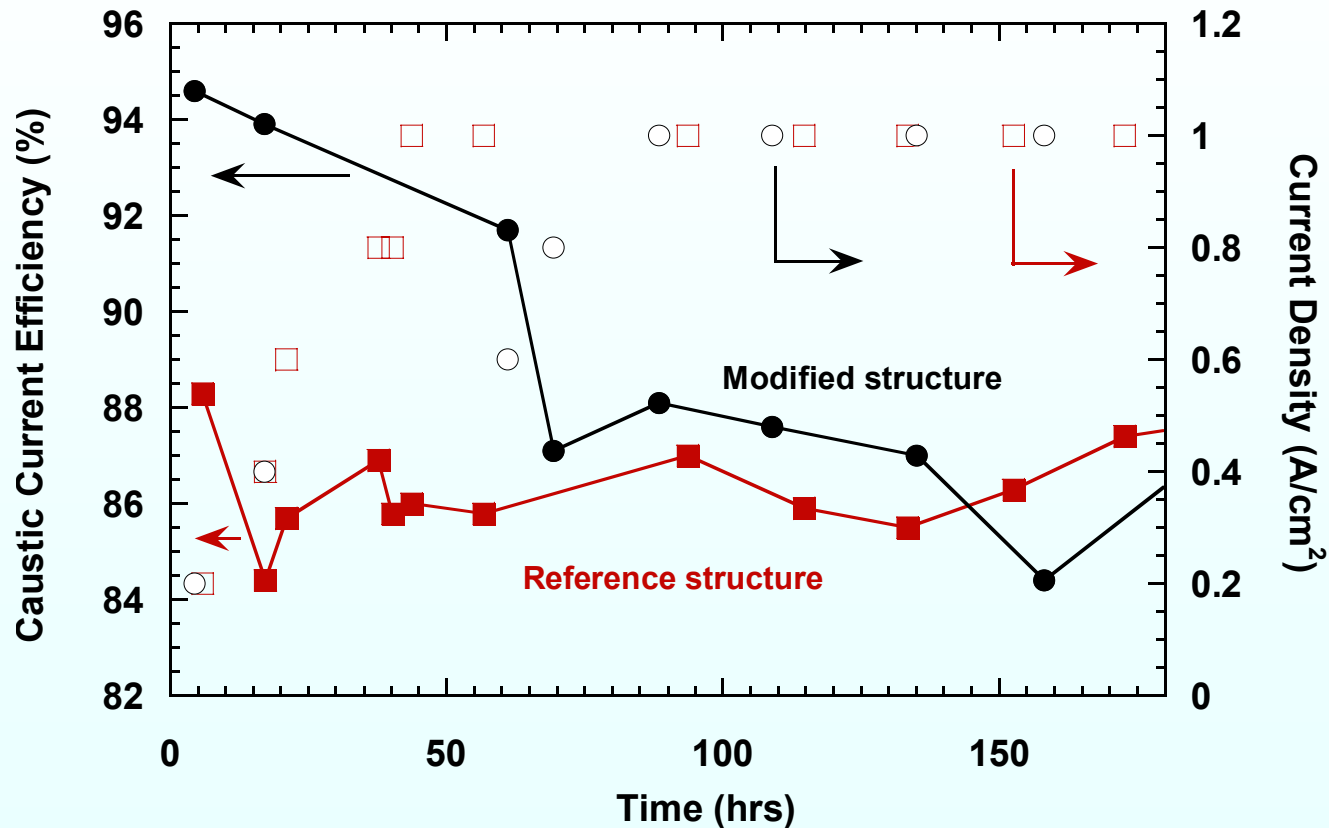
Effect of Cathode Hardware Coating On Peroxide Generation

Silver plated hardware is less effective as peroxide decomposition catalyst than gold plated hardware



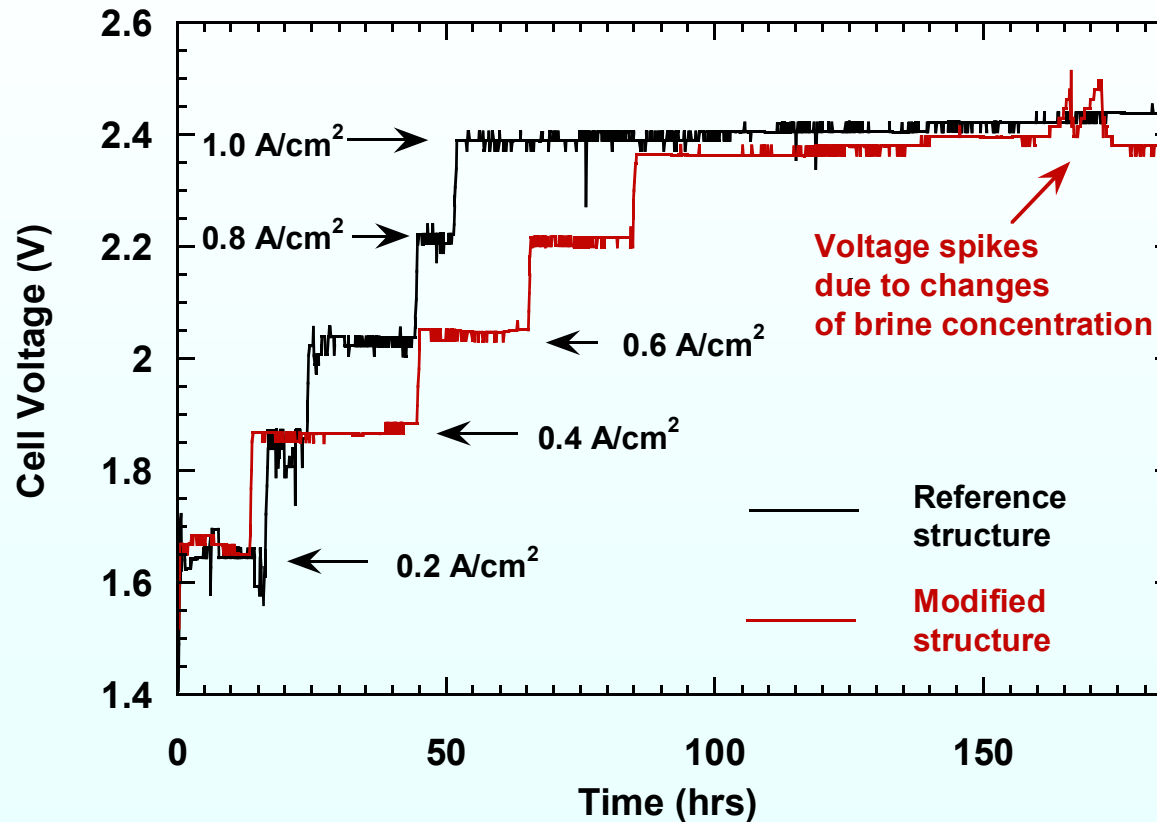
Effect of Cathode Modification on Caustic Current Efficiency (CCE)

Higher CCE for modified structure at lower throughputs ($j \leq 0.6 \text{ A/cm}^2$)
No effect at higher throughputs ($j \geq 0.8 \text{ A/cm}^2$)



Effect of Cathode Modification on the Cell Voltage

Small decrease of the cell voltage at highest current densities



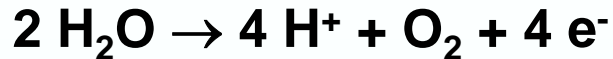
Cathode Hardware Corrosion

- **Gold plated stainless steel (316) hardware**
moderate corrosion under **open circuit** conditions,
very slight corrosion under the cathode gasket during
electrolysis
- **Gold plated nickel hardware**
severe corrosion under **open circuit** conditions, **non-**
negligible corrosion under the cathode gasket during
electrolysis
- **Silver plated nickel hardware**
excellent corrosion **resistance** under **open circuit**
conditions and during **electrolysis**



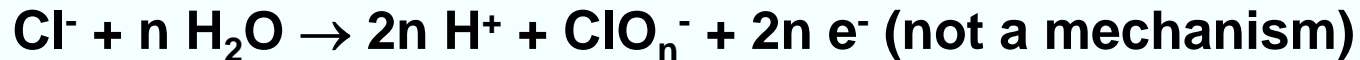
Anode Side Processes Leading to Lowering Caustic Current Efficiency (CCE)

- **Oxygen evolution**



Excess of H^+ is transported through the membrane to the cathode compartment, where it neutralizes OH^-

- **Chlorine oxo-anion formation**



Same effect as for O_2 evolution

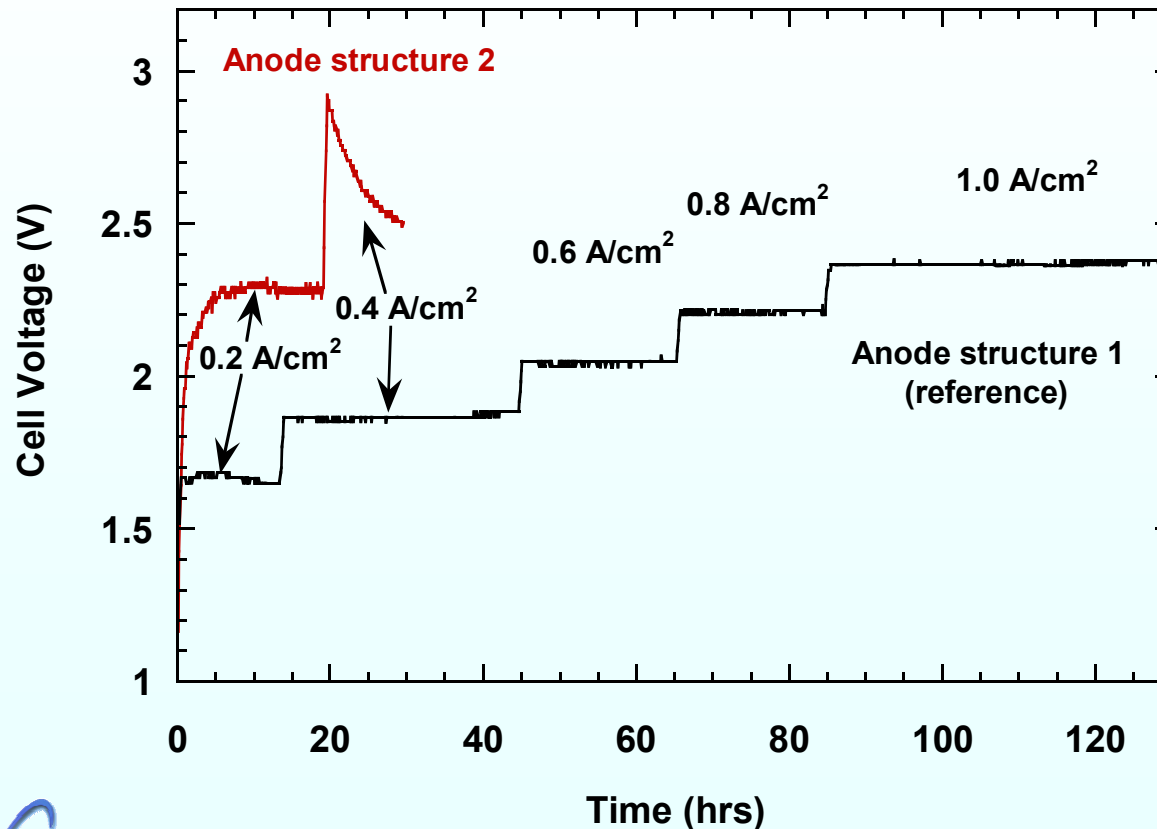
- **Membrane blinding** by chlorine gas

Local current densities higher than the membrane was designed for lead to increased membrane permeability and higher NaOH crossover

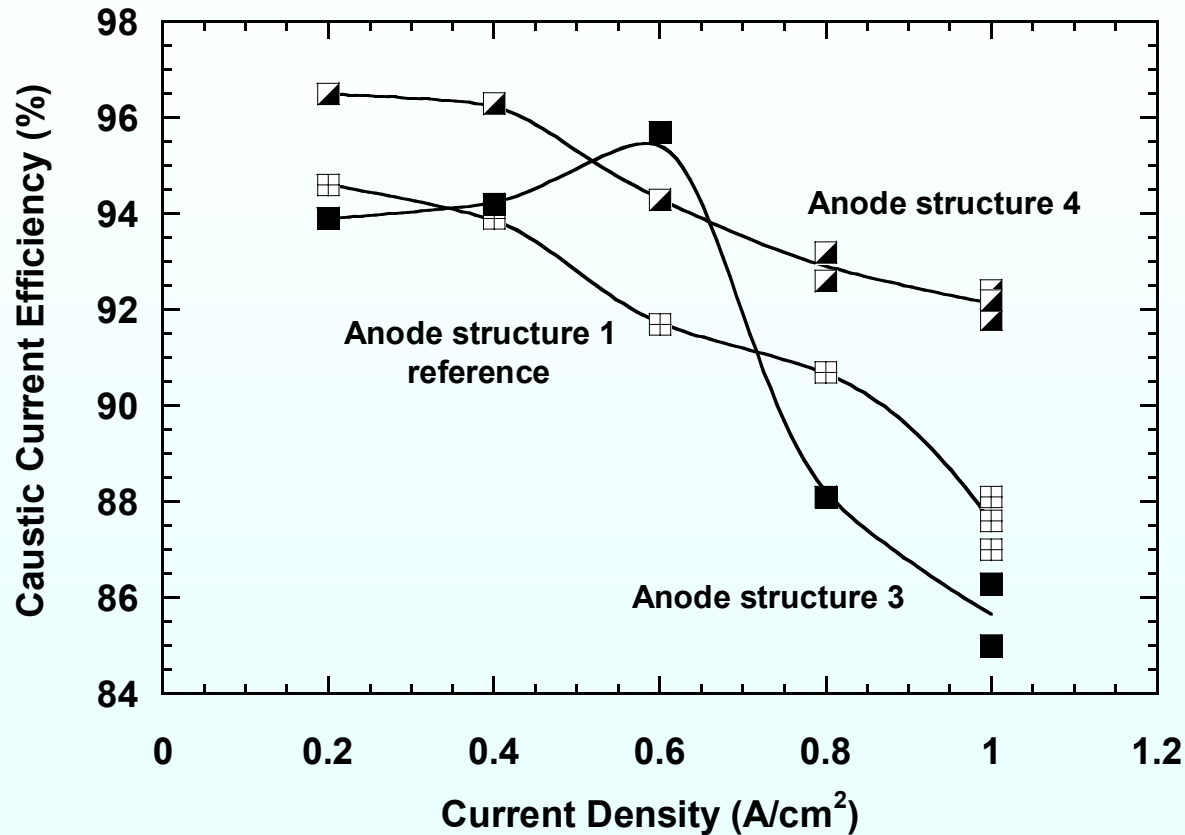
Anode Modifications Aimed at Improving CCE

Material Compatibility Issue

Structure 2 failed as a result of incompatibility of the material used.
High cell voltages accompanied by low caustic current efficiency



Improving Caustic Current Efficiency (CCE) Through Anode Modifications



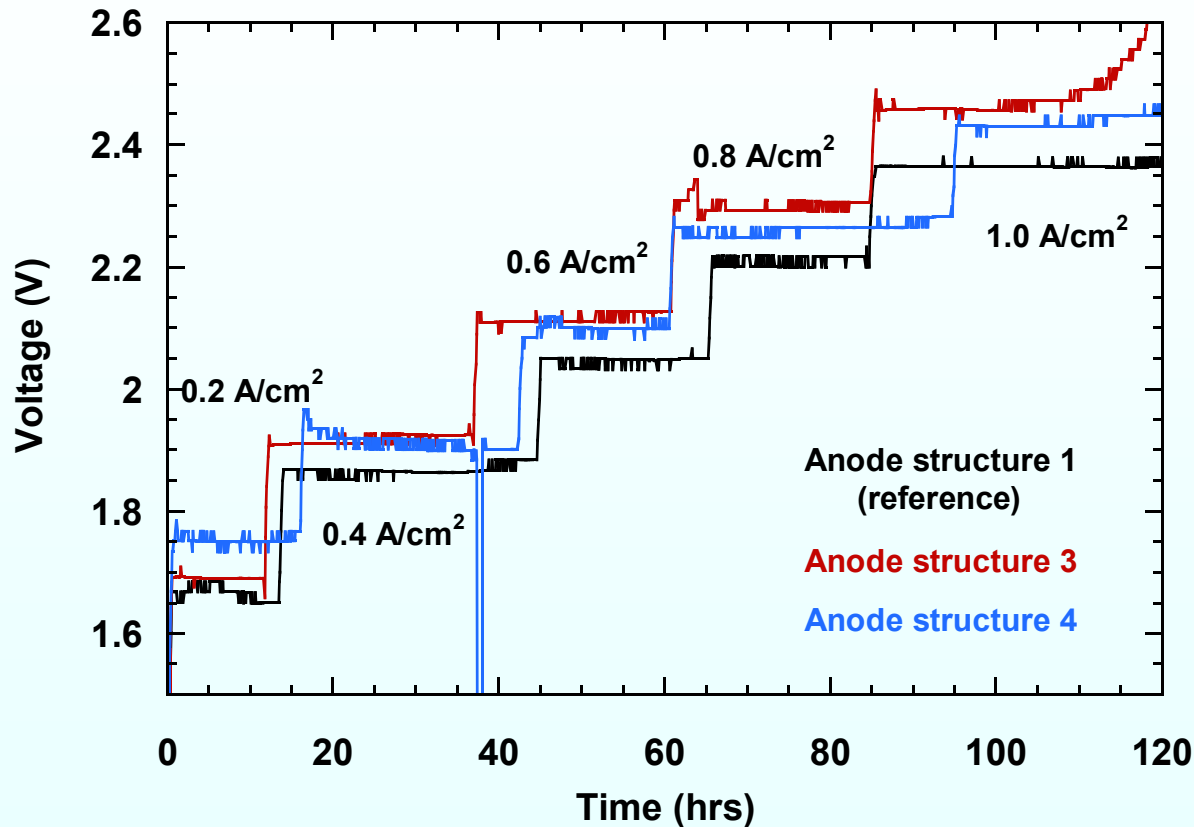
Structure 1 – original, unmodified

Structure 3 – improves caustic current efficiency at $j \leq 0.6$ A/cm², invention disclosure submitted

Structure 4 – improves caustic current efficiency at all current densities, invention disclosure submitted

Effect of Anode Modification on the Cell Voltage Structures Improving CCE

Structures 3 and 4 offer increase of CCE at a relatively small penalty in cell voltage
Structure 4 exhibits better overall performance – lower cell voltage, high CCE at all current densities



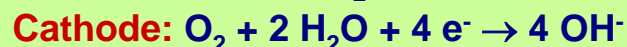
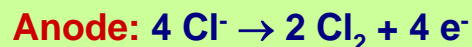
Future Plans

- **Membrane testing:**
select the best membrane in terms of overall performance, *i.e.*, cell voltage, current efficiency, product purity (already started)
- **Testing unsupported catalysts:**
Reduce catalyst loss
- **Anode flow-field modifications:**
Design an inexpensive scalable anode flow-field

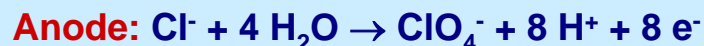
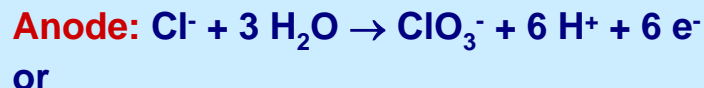
Industrial Use of Gas Diffusion Electrode Technology

Electrolytic Reactors

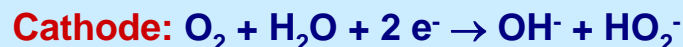
Chlor-Alkali



Chlorate, Perchlorate



Hydrogen Peroxide

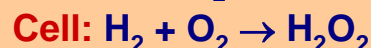
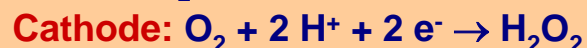
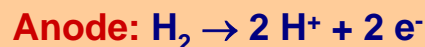


HCl Destruction

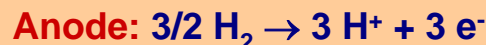


Fuel Cell Type Reactors

Hydrogen Peroxide



Hydroxylamine



Selective Hydrogenation of Unsaturated Compounds

Waste Treatment

Pilot Plant

Possible

R@D

Participants, Funding & Acknowledgements

Project Participants

Los Alamos National Laboratory
PPG

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